

Low Temperature Thermal Analysis of TC410 Resin Prepreg and Laminate System

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Abstract

TC410 resin prepreg is an advanced engineering material, one of the composite materials used in the fabrication of structural panels for satellites. The low temperature thermal analysis performed by using Differential Scanning Calorimetry (DSC) and Modulated DSC (MDSC) has revealed that the material exhibits reversing glass transition around -50°C and non reversing endothermic relaxation between -35°C to -65°C range. The dip at 0°C indicates water traces which might be due to moisture content on the surface. The study brings out that the system is thermally stable. All the results are found to be repeatable and reproducible within 3% uncertainty.

Keywords

Prepreg; Laminate; TC410; DSC; MDSC; Glass Transition; Thermal Analysis

Introduction

TC410 is a recent high performance cyanate ester resin composite system developed by Tencate. It is specifically designed for the current generation radomes and satellite structures. The key properties of TC410 are (i) low curing temperature that of 121°C, (ii) low moisture absorption and (iii) high conversion levels. It reduces the stress that occurs during part fabrication and provides good resistance to radiation, which has low micro cracking and excellent resistance to process moisture. Also TC410 has low dielectric and loss tangents.

Thus, TC410 has all the potential characteristics that are necessary for satellite fabrication. Also, recently developed TC410 to be used as a matrix material in composites for space applications shows increase in bondability because of atmospheric plasma treatment (APT). It is an effective surface preparation technique for adhesive bonding and is used on a number of composite systems. In ISAC, it is being used in realizing different panels of various satellites.

TC410 prepreg procured from Tencate for in-house

panel fabrication purposes. In general, prepreg are rolls of uncured resin materials in which the fibers have been pre-impregnated with the resin. The process of lamination involves layup of the prepreg to the desired orientation/ thickness, followed by heat and pressure operation which cures the resin and forms the laminate. Also one should note that the prepreg resin gets fully cured only by heating them to the prescribed cure temperature-time profile.

The literature delineates that at positive temperature, TC410 resin has low stress free cure temperature, less moisture sensitivity, and low CTE and CME. But nothing is spelt out about its low temperature behaviour especially below 0°C. In reality the panels of satellites are exposed to temperature variations in the temperature range of -100°C to +100°C depending on the orbital variation/ location. Hence, carried out a study to establish the thermal behaviour of TC410 resin composite system at sub zero temperatures with the help of proven conventional Differential Scanning Calorimetry (DSC) and sophisticated Modulated DSC (MDSC) methods.

DSC is a technique which measures the heat flow into or out of the material as a function of temperature. It provides the quantitative and qualitative information about the material such as presence of various transitions like glass transition, crystallization, curing, melting and decomposition. This data is generally obtained from a conventional DSC. Here, the specific heat capacity (CP) is proportional to the resulting heat flow response, normalized for sample mass and heating rate, expressed as;

$$C_p = K \times \frac{HF_s - HF_{MT}}{R \times M} \quad (1)$$

Where, K is DSC Calibration Factor, HF is Differential heat flow with sample and empty pans , R is heating rate and M is sample weight.

Whereas, MDSC is the most effective, unique and emerging technique in which the test specimen is exposed to a linear heating method which has superimposed sinusoidal oscillation, resulting in cyclic heating profile. The resultant experimental heat flow during the cyclic treatment provides not only the total heat flow usually obtained from conventional DSC, but also separates the total heat flow into its reversing (heat capacity) and non-reversing (kinetic) components. The other benefit of this measurement includes improved resolution of closely occurring or overlapping transitions, higher sensitivity for weak transitions, its' ability to determine the initial crystallization, and direct measurement to heat capacity.

Inbuilt data analysis software of MDSC automatically calculates and directly plots heat capacity results. Further for MDSC measurement, similar conventional DSC cell arrangement is used, but a different heating profile is applied to the sample and the reference by the furnace. The mathematical representation of heat flow equation of a typical heat flux of DSC in MDSC mode is:

$$\frac{dQ}{dt} = \underbrace{(C_p + f_R(t, T))}_{\text{reversing}} \frac{dT}{dt} + \underbrace{f_N(t, T)}_{\text{non-reversing}} \quad (2)$$

where dQ/dt is total heat flow, dT/dt is heating rate, C_p is heat capacity of the sample and $f_R(t, T)$, $f_N(t, T)$ correspond to function of time and temperature which govern the kinetic response of any physical or chemical transition. Thus, conventional DSC measures only total heat flow whereas, MDSC measures total heat flow and also reversing and non reversing thermal events separately.

In-depth thermal analysis, especially at low temperature studied on prepgs as received TC410 and cured TC410 resin laminate systems. The prepreg sample which cured inside a DSC cell adhering to the procedure as specified in Tencate literature carried out. The material used in panel fabrication is expected to be thermally stable in the temperature range of -100°C to +100°C. The material characterization happens at a range of -125°C to +125°C, three test specimens namely virgin TC 410 prepreg, cured laminate and the prepreg cured in DSC has been characterized by means of conventional DSC and by MDSC techniques. All measurement results are found to be repeatable and reproducible within a deviation of 3%.

Experiment

DSC measures the difference in heat flow between an unknown sample and selected reference sample as a function of temperature. Firstly, the sample to be tested is weighed precisely, sealed and crimped in a standard pan with the help of the press so that the sample does not get oxidised during the programmed heating process. 99.999% pure Helium is used as sample purge gas and 99.999% pure Nitrogen is used as base purge gas for better baseline stability as well as to avoid oxidation of the sample or atmosphere interactions.

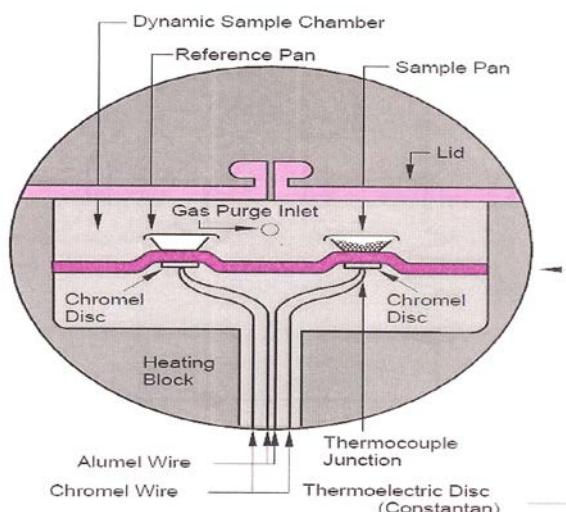


FIG. 1 SCHEMATIC OF HEAT FLUX DSC CELL

The heat flux DSC cell as shown in Fig.1, designed on Tzero technology assures precise isothermal furnace operation. ANSI grade Chromel-constantan thermocouples located symmetrically between the sample and the reference platforms acts as an independent measurement and cell bottom side thermal control sensor. The matched chromel area thermocouples mounted to underside of the raised sample and reference platforms of single piece thin constantan disc lead to faster signal response, flat baseline, improved sensitivity and data precision. Based on the test specimen and reference details, absolute values of the heat flow and heating rate the C_p was calculated automatically by the inbuilt software of the system.

In the present study, Q100 DSC instrument is used. The purpose of using this thermal analyzer is to determine the transition temperatures of the sample. And to make this information meaningful in an absolute sense, it is important to work out temperature calibration of the instrument and comparison of the measured data to that of known certified standard

material.

Therefore Q100 DSC was calibrated for temperature as per ASTM E967-03 two point calibration procedure with NIST Standard Reference Materials (SRMs) Indium (M.P 156.61°C; Heat of fusion 28.71 J/g) and Zinc (M.P 419.53°C; Heat of fusion 108.0 J/g) before the measurements. As a performance verification run after calibration, measurement of Tin (M.P 231.95°C; Heat of fusion 60.6J/g) was carried out. All DSC measurements were done in sealed (crimped) aluminium containers (cups) of fixed capacity. This helped to determine the effect of containment and its compatibility to the envelop material.

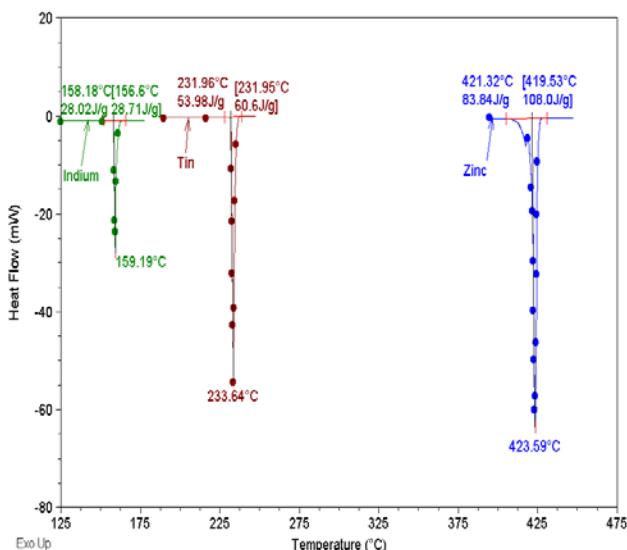


FIG. 2 CALIBRATION & VERIFICATION CHARACTERISTICS OF Q100 DSC

The two point temperature calibration and performance verification characteristics for Q100 DSC is furnished in Fig.2. The measured melting points of the two SRMs by Q100 DSC during calibration are of about 1.8°C more than the certified values. The verification measurement after calibration unambiguously confirms the temperature accuracy wherein the measured value of Tin's MP is less by 0.01°C with respect to certified value.

For TC410, the measurement performed between -125°C to +125°C in DSC with the help of an automated Liquid Nitrogen Cooling Accessory (LNCA). So, to validate the DSC measurement, first measurement performed on certified NIST SRM 720 synthetic sapphire sample. Fig.3. represents specific heat measurement values of sapphire as a function of temperature along with literature (certificate) value.

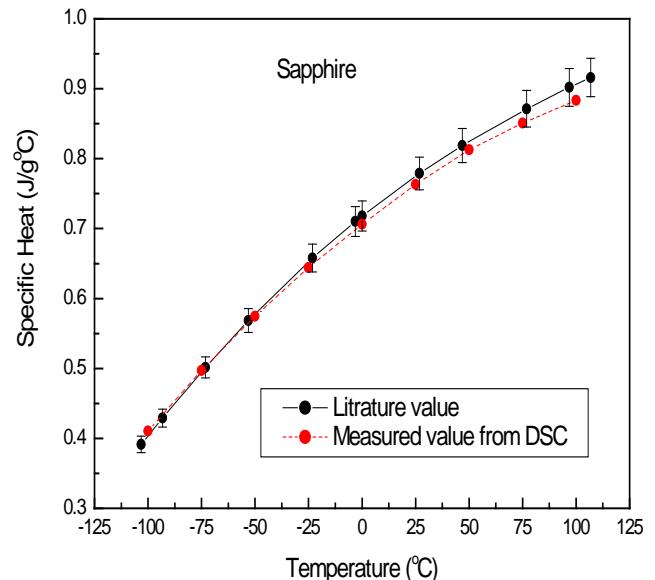


FIG. 3. THE SPECIFIC HEAT OF NIST SRM SAPPHIRE SAMPLE FROM LITERATURE AND DSC MEASUREMENT. THE ERROR BAR SHOW THAT MEASURED VALUE BY DSC EXPERIMENT IS WITHIN 3% UNCERTAINTY

The result clearly reveals that the measured data are in good agreement with reported one and are within 3% uncertainty. This illustrates the reproducibility of the DSC measurements. For every unknown material measurement three samples were taken and each run was repeated for three times without disturbing any of the experimental parameters so that accuracy, repeatability and reproducibility of the measurement can be verified and demonstrated. Further, release of surface adsorbed moisture, process induced stress relaxation are generally noticed in the 1st run and are absent in the subsequent 2nd and 3rd runs. While carrying out measurements using conventional DSC mode, heating rate was selected as 5°C/min whereas, in MDSC mode it was selected as 3°C/min as per OEM recommendations.

Results

TC410 Laminate

The measurements are performed on the TC410 laminate sample used in panels of the satellite and the results are shown in Fig. 4 in the temperature range -125°C to 125°C. Around -50°C an endothermic transition is observed with a small dip in the heat flow graph, which is stable and repeatable in every heating cycle. In cooling cycles the same thermal event shifts to further lower temperature and occurred at -75°C though not so prominently visible. To check the reproducibility of the thermal events, 5 consecutive heating and cooling cycles are performed without

disturbing the experimental setup/parameters and found that similar thermal events are present in all cycles. Very little deviation in transition position is noticed in every individual cycle which is very much within the measurement accuracy of DSC. The study indicates that observed thermal events in TC410 system is repeatable, reproducible and is thermally stable.

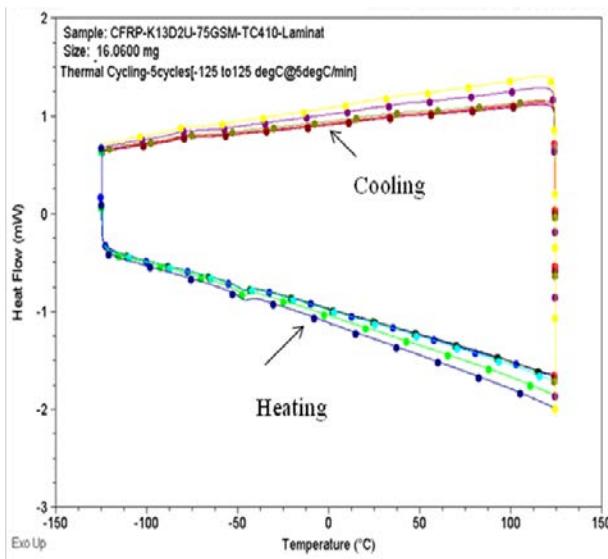


FIG. 4. THE HEAT FLOW MEASUREMENTS OF TC410 RESIN LAMINATE SYSTEM AS A FUNCTION OF TEMPERATURE FOR 5 HEAT/COOL THERMAL CYCLES IN DSC Q100 AT A RATE OF 5°C/ MIN

Fig. 5 furnishes the heat flow behaviour for one heating cycle only with its derivative plot. The plots clearly indicate the presence of an endothermic thermal event followed by an exothermic transition between -65°C to -35°C.

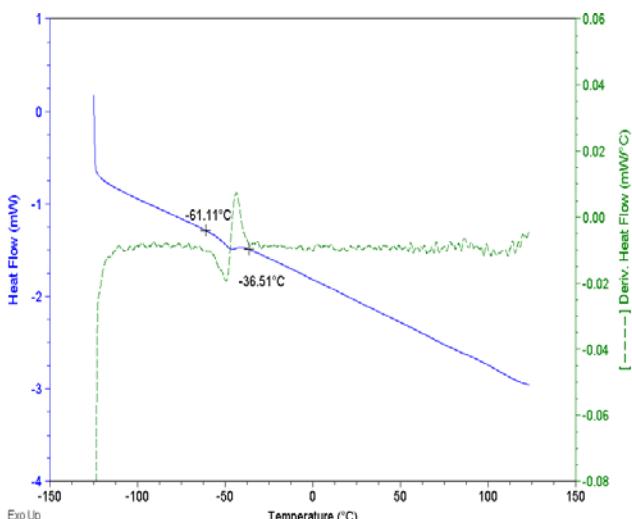


FIG. 5. THE HEAT FLOW (BLUE) MEASUREMENT AND DERIVATIVE OF HEAT FLOW (GREEN) OF TC410 LAMINATE SAMPLE AS A FUNCTION OF TEMPERATURE.

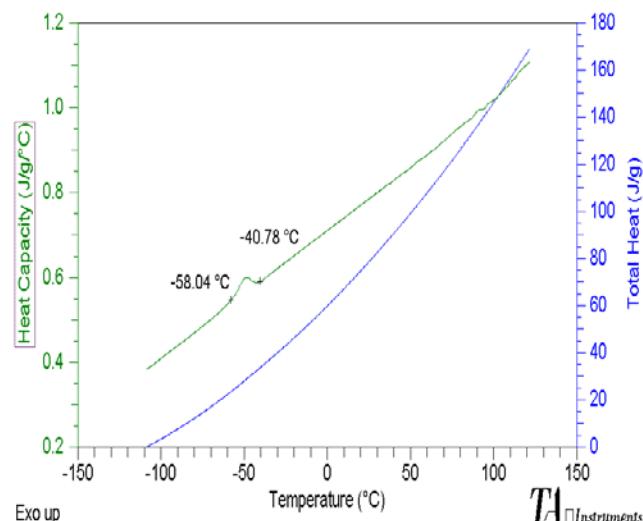


FIG. 6. THE HEAT CAPACITY (GREEN) AND TOTAL HEAT (BLUE) OF TC410 LAMINATE SAMPLE AS A FUNCTION OF TEMPERATURE

Based on the sample and reference details, such as, absolute heat flow and heating rate, the heat capacity values for TC410 laminate was obtained with the help of the inbuilt software utility. To arrive at heat capacity value the software subtracts reference and baseline heat flow value from total heat flow of the sample. Fig. 6 presents the heat capacity and total heat flow of the first run of the TC410 laminate sample as a function of temperature. The exothermic peak around -50°C is quite pronounced, clearly illustrate that this behaviour is because of some intrinsic property. Thus, the heat capacity graph clearly revealed that the thermal event around -50°C corresponds to glass transition (T_g). This T_g might be due to TC410 prepreg behaviour or due to any one of the constituent component in TC410 prepreg resin. However, it is very difficult to attribute this phenomenon to any of the constituents of TC410 as its composition is proprietary of the manufacturer.

TABLE 1. HEAT CAPACITY VALUES OF TC410 LAMINATE FOR ALL 3 RUNS AS A FUNCTION OF TEMPERATURE

Temperature (°C)	Laminated TC410 sample (wt=36.150gm)		
	1 st Run	2 nd Run	3 rd Run
-100	0.409	0.406	0.401
-75	0.485	0.481	0.475
-50	0.597	0.589	0.587
-25	0.637	0.630	0.624
0	0.712	0.704	0.698
25	0.786	0.777	0.771
50	0.859	0.851	0.844
75	0.940	0.926	0.916
100	1.018	0.999	0.991

The Table.1 presents Heat capacity data of TC410 laminate as a function of temperature for all 3 consecutive runs. The measured data demonstrate the raise in Cp with respect to rise in temperature. Decrease in Cp values of the same sample from 1st to 3rd run substantiates the role of surface adsorbed moisture and process induced stress relaxation phenomena.

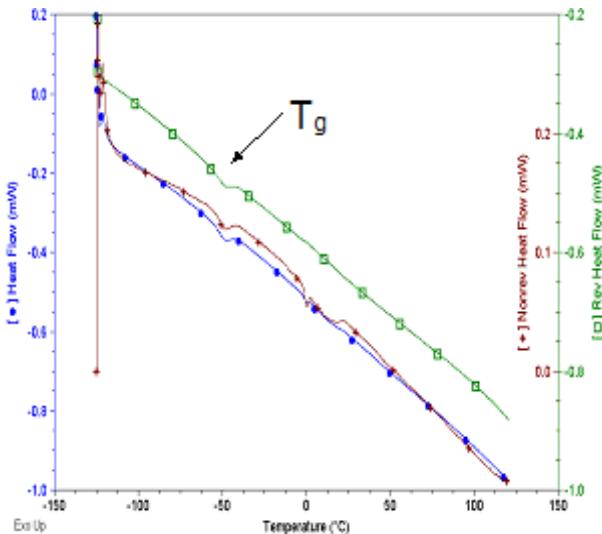


FIG. 7. THE MDSC HEAT FLOW MEASUREMENTS OF TC410 LAMINATE RESIN SYSTEM AS A FUNCTION OF TEMPERATURE .FIGURE ILLUSTRATE HEAT FLOW (BLUE), NON REVERSING (RED) AND REVERSING HEAT FLOW (GREEN) WITH TEMPERATURE

In order to understand the transition better, a measurement performed in MDSC mode of DSC instrument. Fig. 7 shows the Modulated DSC measurement of TC410 laminate sample. The graph furnishes the total heat flow, reversing heat flow and non reversing heat flow behaviour of the sample with temperature. The start up hook observed at -125°C is generally seen in all thermal measurements. The MDSC measurement has separated the glass transition feature which is actually a reversing thermal phenomenon from the endothermic relaxation which is a non reversing phenomenon at around -50°C. A dip appearing at 0°C in non reversing plot is due to presence of moisture content. Thus the MDSC measurement provides better understanding of thermal events in the test sample being investigated. In the present studies, it not only resolves the overlapping transitions but also identifies the weaker transitions.

Further, in order to check whether this transition might be due to lamination process, it was decided to do the measurements on uncured virgin prepreg and then after curing the prepreg sample in DSC cell itself.

TC410 Prepreg

The measurement was performed on the virgin TC410 prepreg sample in the same temperature range of -125°C to +125°C. Fig.8 represents the exothermic stability graph of uncured virgin TC410 prepreg sample as received from the manufacturer.

Here too the transitions around -50°C is noticed in both heating and cooling cycles but not much pronounced as in TC410 laminate sample. Hence rules out the case that the transition present might occur due to lamination process.

Also, in comparison with TC410 laminate sample, the heat flow value is lesser as mass taken for the measurement is smaller. Same as in TC410 laminate sample, transitions is found to be shifted to lower temperatures during cooling cycle. The thermal event around 0°C is due to the surface absorbed moisture in process or in storage.

The broader peak substantiates the manufacturers claim that TC410 is comparatively a less moisture prone system. Whereas, the exothermic thermal fluctuations noticed above 100°C in both heating and cooling cycles indicate that the test sample is not fully cured. It is to be noted that curing procedure at temperature 121°C and time recommended by Original Equipment Manufacturer (OEM) not adopted in this case.

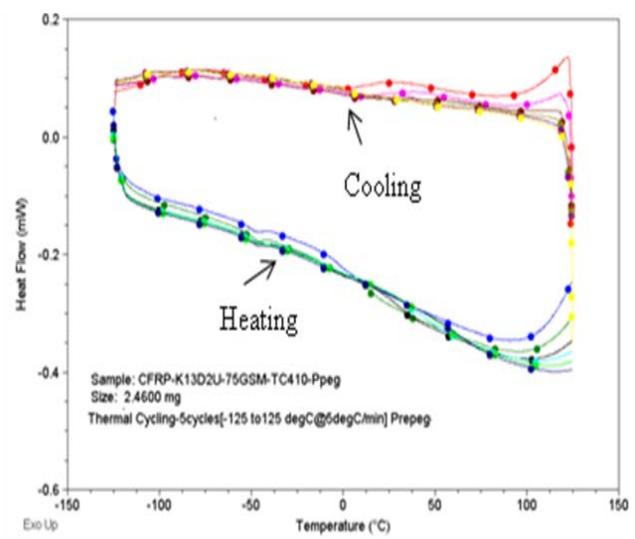


FIG. 8. THE HEAT FLOW MEASUREMENT OF VIRGIN TC410 RESIN PREPREG SYSTEM AS A FUNCTION OF TEMPERATURE FOR 5 THERMAL CYCLES IN DSC Q100 AT A RATE OF 5°C/ MIN

TC410 Prepreg Cured in DSC

In this study, for curing the above TC410 prepreg sample, same temperature profile was employed as

specified in the manufacturer's literature. The sample was kept in DSC furnace and programmed as per the recommended curing temperature profile as shown in Fig 9.

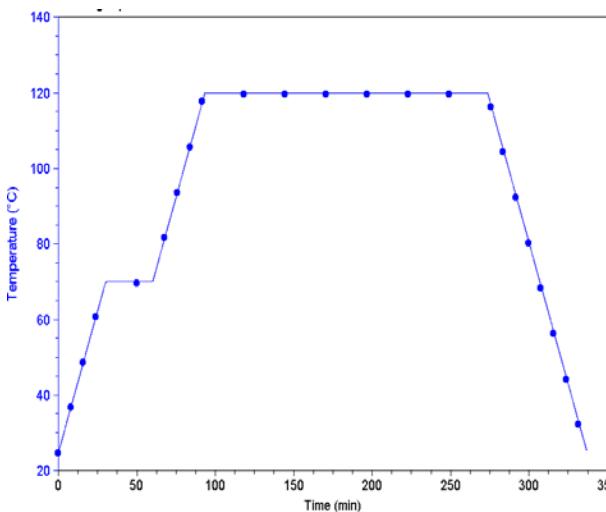


FIG.9. THE OEM RECOMMENDED TIME-TEMPERATURE PROFILE FOR CURING TC410 PREPREG SAMPLE

From room temperature the sample was heated up to 70°C at a heating rate of 5°C/min and held at this temperature for 30 minutes. Further it was heated to 120°C at same heating rate and again held for 3 hrs and then finally cooled down to room temperature at the rate of 5°C/min. Later, thermal characterization of the sample was carried out.

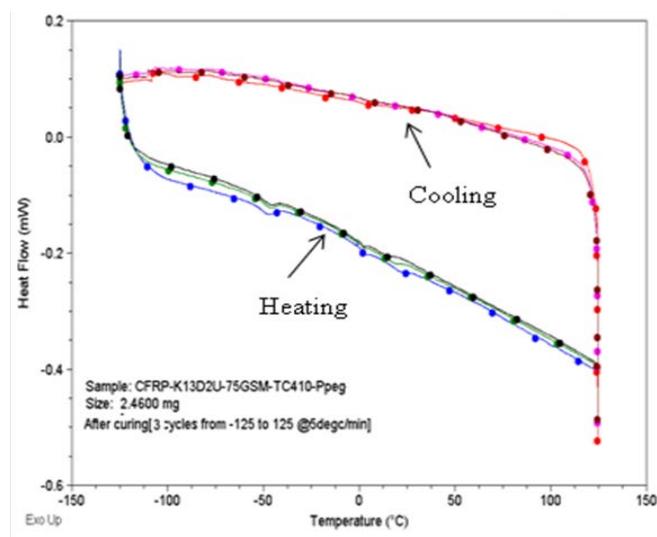


FIG. 10. THE HEAT FLOW MEASUREMENT OF DSC CURED TC410 PREPREG RESIN SYSTEM AS A FUNCTION OF TEMPERATURE FOR 3 THERMAL HEAT/COOL CYCLES

Fig. 10 presents the heat flow measurement of DSC cured prepreg TC410 sample as a function of temperature for three consecutive thermal cycles

between the temperatures -125°C and 125°C. The transition at around -50°C is present in both heating and cooling cycles of heat flow measurements. As discussed earlier, thermal event is also noticed around 0°C due to presence of surface adsorbed moisture in the sample. However the heat flow plots for both cured TC410 laminate and cured TC410 prepreg shown in Fig.4 and Fig.10 look similar and the only difference is 0°C transition which is not present in cured TC410 laminate sample.

Thus, from these studies, it is clear that if the prepreg is not cured properly, it leads to many unwanted thermal activity near curing temperature i.e. around 120°C. The difference in heat flow values is due to the difference in thermal masses of single prepreg and the laminate made out of multiple layers of preps.

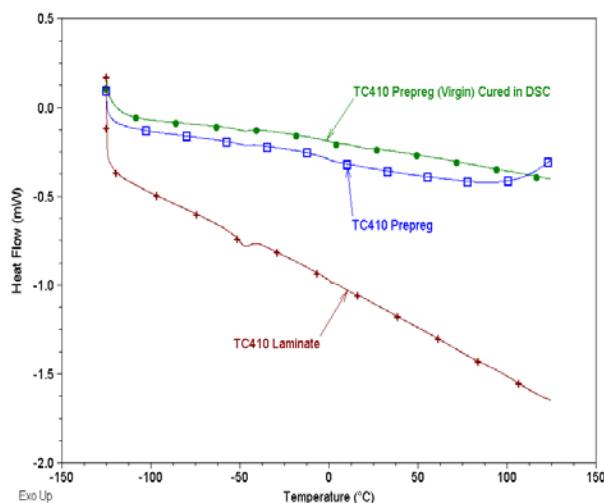


FIG. 11. CURVE OVER LAY OF TC410 PREPREG (VIRGIN) CURED IN DSC, TC410 LAMINATE AND TC410 PREPREG.

Fig. 11 shows the curve over lay of TC410 prepreg, TC410 prepreg (virgin) cured in DSC and TC410 laminate. Low heat flow value with increase in temperature in laminate TC410 sample is due to its multilayer form. The graphs clearly reveal that cured samples of TC410 are more thermally stable compared to the prepreg sample.

Conclusions

To summarize Q100 DSC instrument used for present studies was calibrated and validated for temperature as per ASTM E967-03 two point calibration procedures with NIST Standard Reference Materials before the measurements.

The thermal analysis studies on TC410 prepreg and laminate resin system, revealed the reversing glass

transition around -50°C. The transition is quite stable and is present in both heating and cooling cycle with a slight shift to further lower temperature in cooling. The peak in heat capacity plot confirms the existence of the transition.

However, the results illustrate without doubt that TC410 resin system is very much thermally stable. MDSC measurement not only separated the broad transition of heat flow into the exothermic glass transition from the endothermic relaxation which is a non reversing phenomenon at around -50°C but also identified the weak transition at 0°C noticed in non reversing plot which is due to moisture content in the sample. All the results are repeatable and reproducible with a deviation of about 3% uncertainty.

Thus, the measurements definitely indicate the understanding of TC410 composite system's thermal events especially at low temperature, important in the fabrication and realization of panels for various satellite programs.

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